PolaBer: a program to calculate and visualize distributed atomic polarizabilities based on electron density partitioning

Authors

Anna Krawczuk[a]*, Daniel Pérez[b] and Piero Macchi[b]*

[a]Faculty of Chemistry, Jagiellonian University, Ingardena 3, Krakow, 30-060, Poland

[b]Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, Bern, 3012, Switzerland

Correspondence email: piero.macchi@dcb.unibe.ch, krawczuk@chemia.uj.edu.pl

Synopsis A program is presented for the calculation and visualization of distributed atomic polarizabilities, quantities which are useful for the evaluation of crystal properties such as the optical indicatrix.

Abstract In this paper, we describe the program PolaBer, which calculates atomic polarizability tensors from electric field perturbations of a partitioned electron density distribution. Among many possible partitioning schemes, PolaBer is currently using the quantum theory of atoms in molecules and it is interfaced to programs that apply such a partitioning. The calculation of the atomic tensors follows the idea by Keith (*Atomic Response Properties* in *The Quantum Theory of Atoms in Molecules: From Solid State to DNA and Drug Design*, Eds. Matta, C.F. & Boyd, R.J., Viley-VCH, Weinheim, 2007) that enables removing the intrinsic origin dependence of the atomic charge contributions to the molecular dipole moment. This scheme allows exporting, within chemical equivalent functional groups, properties calculated from atomic dipoles, as for example the atomic polarizabilities. The software allows visualization of the tensors and calculation of straightforward optical properties of a molecule (like the molar refractive index) or a crystal (assuming the molecule in a given crystal lattice).

1. Introduction

The response of an electron density distribution against perturbation is very important to understand the behavior of molecules or solids during chemical reactions or phase transformations, solvation or molecular recognition processes, emission of optic or spectroscopic signals.

If the perturbation is due to an external electric field, the molecular response is controlled by the (hyper)polarizability of the molecule. Quantum chemistry allows to calculate dipolar (hyper)polarizabilities of molecules and crystals by derivation of the electronic energy *E* with respect to the electric field *F*. For example, α_{ij} component of the first order polarizability tensor is defined as:

$$\alpha_{ij} = -\frac{\partial^2 E}{\partial F_i \partial F_j} \qquad (1)$$

Because the derivative of energy with respect to the field corresponds to the dipole moment, α_{ij} can be calculated also as the derivative of the dipolar moment with respect to the field:

$$\alpha_{ij} = -\frac{\partial^2 E}{\partial F_i \partial F_j} = \frac{\partial \mu_j}{\partial F_i} \qquad (2)$$

This means that the polarizabilities are more directly connected to an easy observable like the electron density (more precisely to the moments of the electron density) rather than to the electronic energy, a quantum mechanical observable which is however not easily available from experiments.

Similarly to the charge distribution, a chemist would prefer to analyze the atomic and bond polarizabilities of a system rather than the total molecular quantity. There are many reasons for that. First of all, atoms or functional groups of atoms represent the way in which molecular chemists normally "reduce" a molecule (or a molecular crystal) to rationalize the chemical functions, such as reactivity, molecular recognition, solvation etc. The same could be valid also in material science for engineering purposes. In fact, a given property may originate from a particular functional group of the molecule, therefore it is important to know what is the actual effect of each functional group. In addition, atomic parameterization is a prerequisite for semi-empirical (force field based) modeling of intermolecular interactions, for example in molecular mechanics or molecular dynamics simulations. In this respect, transportable atomic polarizabilities are extremely useful, in analogy with transportable atomic multipolar moments (Pichon Pesme, Lecomte, & Lachekar (1995), Volkov, Li, Koritsanszky *et al.* (2004), Dittrich, Hubschle, Luger et al. (2006) Zarychta, Pichon-Pesme, Guillot *et al.*(2007) *Acta Cryst.* **A63** 108-125).

The breakdown of molecular dipole moment into atomic terms allows calculating the contribution of each atom to the molecular polarizability. Many atomic partitioning schemes have been proposed in the literature. Most of them were intended to distribute the molecular electric moments into atomic terms (Stewart, Bentley & Goodman (1975), Stewart (1976), Hansen & Coppens (1978), Hirshfeld (1977), Kurki-Suonio, K. (1968), Kurki-Suonio, K. (1977)). Stone (1985) and Sueur & Stone (1993) directly analyzed several partitioning schemes of the molecular polarizabilities and concluded that the space partitioned atomic polarizability volumes would be the most efficient. Bader *et al.* (1987), Laidig & Bader (1990), Bader (1989) and Bader *et al.* (1992) also proposed hard space partitioning of the molecular polarizabilities, based on QTAIM, which was later generalized by Keith (2007). Hättig *et al.* (1996) have first proposed the atomic partitioning of frequency dependent polarizabilities, based

on QTAIM as well as on Stone's approaches. Their main purpose was to estimate atom-atom dispersion coefficients for the evaluation of intermolecular interaction energies. Gough *et al.* (1996) have used QTAIM polarizabilities to compute intensities of Raman spectra. However the results of atomic partitioning are missing in that work.

Devarajan & Glazer (1986) and Glazer & Stadnicka (1986) have derived theoretical background to connect anisotropic atomic polarizabilities to some optical properties, like refractive indices and optical rotatory power. In those papers, atomic polarizabilities in crystals were visualized for the first time.

We have recently shown (Krawczuk et al., 2011) that the partitioning proposed by Keith, and implement in AIMAll (Keith (2013)), could be used to solve the problem of origin dependence which affects the partitioning of molecular (hyper)polarizabilities. The problem arises from atomic charges that produce a dipole moment when shifted from the center of charge of the molecule. It should be recalled at this point that the total molecular dipole is origin independent if the total molecular charge is zero. However, as each atom in the molecule is not neutral (unless trivial exceptions), the charge-distance vectors generate an "apparent" origin dependence, which is a "true" one if the molecule is not neutral. Keith proposed to "cancel" the atomic charges translating them into the bonds and creating, at each atom center, additional dipolar terms originated from the bond charge translation, also defined as "directed bond contributions to the atomic charge" by Keith (2007). After this transformation, each atom possesses only dipolar terms: the electric dipole moment calculated from the uneven distribution of charge inside the atomic basin (*atomic polarization*) and the *charge translation* dipole (the sum of all bond charge translation dipoles). The molecular dipole moment is the exact sum of all these atomic terms and the origin dependent charge-distance contribution has disappeared. Even for non-neutral molecules, the dipole remains invariant under a change of coordinate system, if using the same space partitioning of the electron density. The most important consequence of this operation is that the atomic polarizability terms are easier to compute and much more transportable from one atom to a chemically equivalent one belonging to another molecule (even of completely different geometry), which is an important condition for force field approaches in molecular modeling. At the same time, this approach allows a breakdown into atomic components of the terms that give origin to optical properties of a molecule or a crystal, which is important for the design of molecular based materials.

In the following, we will briefly revise the theoretical background and will present the software PolaBer that calculates and visualizes atomic polarizability tensors.

2. Theoretical background

According to the QTAIM partitioning method atomic properties such as atomic charges $Q(\Omega)$, energies E(Ω) or, in particular, dipole moments $\mu(\Omega)$ can be calculated by integrating their corresponding operators over the volume of the atomic basin Ω. The atomic dipole moment can be then defined as:

$$\mu(\Omega) = -\int_{\Omega} [r - R_{\Omega}]\rho(r)dr + \sum_{\Omega'}[R_{\Omega} - R_b(\Omega|\Omega')]Q(\Omega|\Omega') \qquad (3)$$

where $Q(\Omega|\Omega')$ is the charge contributed to atom Ω by the bond to atom Ω′, R_{Ω} is the position vector of atom Ω with respect to an arbitrary origin and $R_b(\Omega|\Omega'')$ is the positional vector of the bond critical point between atom Ω and Ω'. The first part of the equation (3) describes *atomic polarization* $\mu_p(\Omega)$ term, whereas the second part is the *charge translation* $\mu_c(\Omega)$ component. Equation (3) can be then rewritten as:

$$\mu(\Omega) = \mu_p(\Omega) + \mu_c(\Omega) \qquad (4)$$

The atomic polarization term comes from the integration of dipolar density function within the atomic basin and the charge translation term is given by the weighted sum of atomic charge translations from atom's nucleus to each bond critical point (BCP) connected to that atom. The sign and value of charge translation component strongly depend on the nature and number of groups bonded to the selected atom. The atomic polarization is taken directly from partitioning of electron density, whereas the charge translation component is computed adopting some constrains. First of all, the sum of net atomic charges must be equal to the molecular charge, which in the simplest case is equal to zero. Each atomic charge $Q(\Omega)$ is expressed by the sum of bond charges $Q(\Omega|\Omega')$:

$$Q(\Omega) = \sum_{\Omega'\prime\neq\Omega}^{N_a} Q(\Omega|\Omega') \qquad (5)$$

where $Q(\Omega|\Omega') = 0$ if Ω and Ω' are not bonded. Furthermore, for each bond:

$$\mathrm{Q}(\Omega|\Omega') + \mathrm{Q}(\Omega'|\Omega) = 0 \qquad (6)$$

If a ring *R* is present in the system, then the sum of bond charges within the ring is equal to zero:

$$\sum_{\Omega\in R} Q(\Omega|\Omega+1) = 0 \qquad (7)$$

where Ω is an atom belonging to the ring *R*. To avoid drastic changes of the shape and values of atomic polarizabilities caused by a presence of weak intra- and intermolecular interactions, PolaBer uses a weighting scheme which is inversely proportional to the bond strength measured, for example, by electron density at BCP:

$$\lambda(\Omega|\Omega+1) = \frac{1}{\rho(\Omega|\Omega+1)} \qquad (8)$$

Thus the equation (7) is rewritten as:

$$\sum_{\Omega \in R} \lambda(\Omega|\Omega+1) \cdot Q(\Omega|\Omega+1) = 0 \quad (9)$$

If no ring is present in a system, equations (5) and (6) produce (N_a + N_b −1) linearly independent equations. The ring conditions add as many independent equations as rings found in the structure. After solving set of equations we obtain bond charges which are then used to calculate *charge translation* terms of atomic dipole moments and thus total atomic dipole moments.

Atomic polarizabilities are numerical derivatives of the corresponding atomic dipoles with respect to applied field. Calculations are carried out numerically and thus:

$$\alpha_{ij}(\Omega) = \frac{\mu_i^{\varepsilon_j}(\Omega) - \mu_i^0(\Omega)}{\varepsilon_j} \quad (10)$$

where $\mu_i^{F_j}(\Omega)$ is the atomic dipolar component along the i direction computed with a given electric field (0 or ε) in direction j. In general, PolaBer uses calculations at $\pm \varepsilon_j$ and computes derivatives by averaging two dipole differences. Moreover, ε is a sufficiently small electric field (typically 0.005 a.u.) to guarantee a better extraction of the linear component of the electron polarization. Because the coupling of atomic volumes and atomic charges is not taken into account, the so obtained atomic polarizability tensors may be non-symmetric (whereas, by definition, polarizability is a symmetric tensor). This problem however can be circumvented by decomposing the polarizability tensor into symmetric and antisymmetric terms as recommended by Nye (1985). This procedure reconstructs very accurately the total molecular polarizability (comparing to molecular polarizability derived from analytical double derivative of the energy with respect to the field). In fact, antisymmetric components of atomic polarizabilities cancel each other in a molecular summation.

3. Program description

PolaBer is written in the Fortran 90 programming language. It consists of a main program and a number of subroutines. The program requires atomic charges, polarization dipoles and critical points of the electron density calculated from external programs, with and without an applied electric field. PolaBer uses these entries to calculate the bond charge translation terms defined in eq. 4 and the derivatives of the dipolar terms with respect to the field, hence the atomic polarizability tensors, which are eventually symmetrized. If a unit cell is given, the program will also calculate the crystal refractive indices.

The windows version of the program is available from the website http://www.macchi.dcb.unibe.ch/PolaBer.html. Sources and compiled executables for other platforms are available on request from the authors. Manual with all the functions and commands in the program is attached to the source code. The main code is supported by a visualization tool, ViewTensor, which generates a X3D file representing data in a 3D scene. It is based on view3dscene by Kamburelis (2011). PolaBer can be run either on Linux or Windows platform with the use of ViewTensor tool. The screenshot of ViewTensor is given in Figure 1.

3.1. Calculation options

PolaBer requires the electron density partitioning of an unperturbed and field perturbed molecular system. In principle this step is completely independent, meaning that the electron density could be obtained from calculations as well as from experiments, with whatsoever kind of approximations. In practice, molecular orbital wavefunctions and corresponding electron density partitioning are the most immediate choices. Since polarizabilities obtained with PolaBer are numerical derivatives of the corresponding atomic dipoles with respect to the applied electric field, calculations of wavefunctions should be carried out at zero electric field as well as under a small electric field, *e.g.* 0.005 a.u., directed along $\pm$X, $\pm$Y $\pm$Z, respectively. The value of proposed electric field was proven (Krawczuk *et al*., 2011) to be sufficiently small to obtain good numerical derivative of the dipolar density, except for some systems which requested a smaller field of 0.001 a.u. for more precise evaluation of the atomic polarizabilities. After obtaining a set of wavefunctions for a given system, integration of electron density is needed. This is done by performing QTAIM partitioning with the use of AIMAll (Keith, 2013) or XD2006 (Volkov *et al.*, 2006), after expanding the molecular density in terms of multipoles. Other software could be used of course, but are not directly interfaced at the moment, and their output would require processing in order to provide PolaBer the requested information. For this reason a generalized input file is also accepted (that can be written by any external software). The format and input requests are given in Table 1. A schematic representation of computational steps before entering PolaBer routine is given in Figure 2. An example of a jobfile for launching all calculations, as well as an example of Gaussian input file are included in Supporting Materials. PolaBer starts with reading and importing necessary data from density integration. Following data is read from AIMALL/XD files:

- Atomic charges q(Ω) and coordinates in Cartesian system
- Coordinates of bond critical points (BCPs) and values of electron density and Laplacian on BCPs
- *Atomic polarization* component of atomic dipole moments $\mu_p(\Omega)$

Apart from AIMALL/XD output files, an additional control file is needed (dipolar.inp) which contains instructions and additional information necessary for PolaBer, see Table 2.

After gathering necessary data, PolaBer starts the calculations that are quite rapid. The first step of the procedure is the calculation of bond charges $Q(\Omega|\Omega')$, necessary to obtain *charge translation* components of atomic dipole moments. In this step PolaBer also searches for rings and cages within the molecular system and applies a weighting scheme (see previous section), if requested by the user.

In the next step total atomic dipole moments are calculated at each electric field, therefore atomic polarizability tensors are eventually obtained after symmetrisation of the tensor.

PolaBer calculates also an estimation of the *bond polarizability:*

$$\alpha_{\Omega-\Omega'} = \mathbf{r}^{T}_{\Omega\Omega'} \cdot (\boldsymbol{\alpha}_{\Omega} + \boldsymbol{\alpha}_{\Omega'}) \cdot \mathbf{r}_{\Omega\Omega'} \qquad (11)$$

where $\mathbf{r}_{\Omega\Omega'}$ is a unit vector in the direction of **Ω-Ω'** bond. It is a projection of atomic polarizability tensors along the bond. This definition is "exact", in the sense that it is not a fitted quantity but it comes univocally from the calculated distributed atomic polarizabilities of the system. On the other hand, it is important to stress that in fact the concept of *bond polarizability* lacks a precise definition. Therefore, $\alpha_{\Omega-\Omega'}$ cannot be compared with other bond polarizabilities proposed in the literature, because based on different definitions.

3.2. Output files

Currently, the program prints out following output files:

- bond.out – a common format file containing summary of atomic/bond polarizability calculations
- bond.res – a crystallographic format containing fractional coordinates of a studied system, format the same as the one produced by SHELX program (Sheldrick, 2008). Instead of ADP's, components of atomic polarizability tensors are given, scaled by the factor of 0.1
- bond.x3d – file representing data as a 3D scene which is visualized with locally developed ViewTensor program

Calculated quantities in the output file are summarized in two main tables: atomic and bond properties. Components of atomic polarizability tensors are listed in Cartesian as well as in crystal system defined in the input file (dipolar.inp). The summary of main quantities printed out in the bond.out file is given in Supplementary Materials in Table S1.

4. Applications

4.1. Isolated molecules

To illustrate how PolaBer works, we start with the calculations on the isolated molecules of urea and L-alanine. In order to obtain wave functions for both molecules, *ab initio* calculations were carried out with Gaussian09 package at B3LYP/6-311++G(2d,2p) level. The geometry of urea was optimized, whereas for zwitterionic form of L-alanine coordinates were taken from neutron diffraction data (Lehmann *et al.*, 1972) and kept frozen for further calculations. These geometries were then used to calculate the wavefunctions under electric field perturbation, using of course the same level of theory. Topological analysis and integration of the electron density in the atomic basins were carried out using AIMAll, (Keith (2013).

Graphical representation of the calculated atomic polarizabilities for both urea and L-alanine molecules is given in Figure 3. The analysis of both schemes indicates a number of features which are characteristic of atomic polarizabilities. First of all the electron density polarization strongly affects also the polarizability. This is evident especially in the direction of stronger chemical bonds. In fact, polarizability ellipsoids are strongly elongated towards more polarizable atoms (see C=O and C-N bonds) and the higher the difference of electronegativity between bonded atoms is, the more prolated polarizability ellipsoids are along the bond. In case of H-atoms values of polarizability tensors are very small compared to non-H atoms (see any H−X bond), which is due to the small electronic population of H-atoms. Nevertheless, it is quite clear that the largest component of polarizability tensor of any H-atom is in the direction of a H−X bond. For urea, values of atomic/molecular polarizabilities obtained with PolaBer are summarized in Table 3. Note that the polarizability tensors fulfil symmetry requirements of the molecule.

4.2. Supramolecular assemblies

We now analyze the influence of interatomic interactions on the shape and orientation of polarizability tensors. Let's first consider two molecules of urea interacting through N–H…O hydrogen bonds (HB). From Figure 4a, we can see that the ellipsoid representing polarizability tensor of O2 atom (acceptor of both HBs) is modified due to hydrogen bonds (compare with the Figure 3a). Since HBs are symmetrically equivalent, the pronounced elongation of oxygen ellipsoid is directed along bisector of ∠N11C9N14 towards C9–O10 carbonyl group. When hydrogen atoms are involved in HBs, the orientation of their ellipsoids changes (with respect to the isolated molecule), towards the acceptor of both hydrogen bonds.

If urea is surrounded by three other molecules and the O2 atom is involved in four instead of two hydrogen bonds of N–H…O type (Figure 4b), the oxygen polarizability tensor behaves differently. Whereas the elongation of the ellipsoid towards C9–O10 bond is comparable to the previous example, the presence of two additional HBs in a plane perpendicular to urea (C1–O2 bond) flattens the ellipsoid into a disc like shape. In case of C9 atom the anisotropy of the tensor is much more affected by the presence of hydrogen bonds (along the O2 atom) than in case of only two urea molecules: the

ratio between the largest and smallest components α33/α11 is 1.51 for cluster build of four molecules, whereas for two molecules it is 1.12.

When we consider a larger cluster where urea is surrounded by all possible hydrogen bonded molecules, see Figure 4c, we observe that the polarizabilities of the central molecule are not enormously different from those in the single HB dimer. In fact, only the polarizabilities of the nitrogen atoms (N3, N6) are significantly changed since they are additionally involved in two hydrogen bonds with O34 atom. What is more interesting in this example is how the direction and strength of the hydrogen bond affects the shape and orientation of ellipsoids representing polarizability tensors of oxygen atoms. For example, if we consider atom O42, the presence of HB towards H7 atom rotates the ellipsoids in the direction of the bond and makes it less elongated in the C–O bond comparing to isolated state. In contrary, oxygen O34 becomes more anisotropic along C–O bond due to the formation of two symmetrically equivalent hydrogen bonds, whereas oxygen O10 behaves like the one from isolated molecule since it is not involved in any intermolecular interactions.

4.3. Crystals

One of the main applications of distributed atomic polarizabilities is the estimation of crystal optical properties. The crystal dielectric constant can be calculated from the atomic polarizabilities. In first approximation, it could be simply the sum of unperturbed polarizabilities calculated in gas phase. However, this would highly underestimate the dielectric tensor, ignoring the enhancement of the polarizability in the field generated by other molecules. The corresponding crystal refractive indices would also be underestimated. The advantage of distributed atomic polarizabilities is that one can calculate a molecule embedded in a cluster of surrounding molecules, as described in the previous paragraph, then easily extract the polarizability of just the central molecule (taking advantage of the atomic distribution) and eventually use this central polarizability to calculate the crystal properties. This approach enables to account at least for the perturbation of the first coordination sphere, which may be more than just a classical electrostatic interaction, especially for crystals with a strong hydrogen bond network. A second correction would be then the account for the long range interactions that can be safely approximated with a simple electrostatic perturbation and treated in classical terms, basically applying the Clausius Mossiotti theory or the anisotropic Lorentz field factor approach. The more comprehensive theory for this approach was provided by Dunmur (1972), Cummins *et al.* (1976) and Bounds & Munn (1981). Jayatilaka *et al*. (2009) and Whitten, Jayatilaka & Spackman (2006) have shown the advantages of this method, testing molecular polarizabilities calculated at different quantum mechanical levels, including X-ray constrained wavefunction. Again there could be an advantage using the distributed atomic polarizabilities: in fact it was noted that a perturbation calculated to a "central" polarizability was not so adequate, in particular if the molecule and the crystal packing are quite anisotropic. For this reason, Bounds & Munn (1977) suggested to

"distribute" the molecular polarizability of the central molecule on different sites, thus enabling a more accurate description. However, the distribution proposed was a simple equi-partition of the molecular tensor on some atomic sites, whereas it is clear from our examples that the atomic polarizabilities are quite diverse and this approach, albeit more precise than a central polarizability approach, may not be sufficiently accurate. Having, instead, the exact atomic polarizabilities, it is possible to perform the calculation with much more precision, using the same formalism of Bounds & Munn (1977).

In Table 4, we report the calculated refractive indices of urea based on: a) the isolated molecular polarizability (here the distributed atomic polarizability is not used); b) the polarizability of a molecule extracted from the first coordination sphere; c) the molecular polarizability computed in a polarizable continuum medium, mimicking the crystal dielectric constant. Calculations a) can be correct by evaluating the interaction of distant molecules using Munn's schemes, namely the so-called Lorentz anisotropic approximation or the rigorous local field approximation (calculated using molecular or distributed atomic polarizabilities). It is notable that the latter approach enables a calculation that is very close to the periodic *ab initio* methods as well as the experimental values, extrapolated at infinite wavelength (Halbout *et al.* (1980).), see Table 4. Combination of molecule in a cluster and Lorentz approach, instead, is not sensible because it would lead to an overcorrection (first coordination sphere counted twice) and quite larger refractive indices. Through the example of Table 4, we just want to illustrate how much of the total enhancement of the dielectric constant is actually due to the first coordination sphere and how much is instead coming from the long range interaction. Indeed, the second part is in fact dominating.

There is an additional calculation shown in Table 4, which is also very interesting to comment: the molecular wavefunction calculated using a dipolar continuum medium, an approach normally adopted in order to simulate the effect of a solvent (c). If the dielectric constant computed for an isolated molecule of urea is used (assuming the same molecular volume as in the crystal), the corresponding crystal refractive indices match almost exactly the experimental ones, without further corrections. This observation is very interesting, because the calculation of distributed polarizabilities for a single molecule of urea within the polarizable medium is just marginally more expensive than the calculation in the absence of such medium and definitely smaller than the calculation of a cluster or the fully periodic system. Of course such calculation does not require Lorentz correction, because implicitly accounted.

5. Conclusions

In this paper, we have reported on a new routine that enables the calculation of distributed atomic polarizabilities form molecular orbital wavefunctions (or in principle also multipolar expansions) of

the electron density distribution of the ground state and the electric field perturbed electron density of a molecule, or in principle of a crystal as well. The program uses an electron density partitioning to define the atomic boundaries. In the illustrated examples, the partitioning is obtained through the QTAIM approach, but other schemes would be equally suitable and will be tested in the future.

One important usage of this approach is the calculation of optical properties in crystals that requires the evaluation of accurate molecular polarizabilities but also of supramolecular perturbations, due to short range interactions within the first coordination sphere, as well as to long range electrostatic perturbations. The calculation of the refractive indices of a crystal is straightforward and in a future work we will also show the evaluation of optical activity and some non-linear optical properties, by extending this approach to hyper-polarizabilities.

Other applications of this method, also useful for crystallographic applications, concern the evaluation of intermolecular induction and dispersion energy terms, within the semi-classical approaches of intermolecular interactions.

Polaber will be developed in the future having these applications in mind.

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Table 1 Format and input requests necessary for entering PolaBer calculations.

Number of atoms: natoms	
At1	Atom label
xyz	Coordinates of At1 given in Å in Cartesian system
Vol	Atomic volume (calculated at ρ = 0.001 au) given in $Å^3$
Q(A)	Atomic charge
Dipole	Cartesian atomic unabridged moments given in Debye/$Å^{(l-1)}$
Quadrupole	
Octupole	
Hexadecapole	
Number of bond: nbond	
At1 At2 xyz rho delrho ellips d1 d2	xyz: coordinates of BCP in Å in Cartesian system
	rho: electron density on BCP
	delrho: Laplacian of electron density on BCP
	Ellips: bond ellipticity
	d1, d2: Distances between At1 and BCP and BCP and At2 given in Å in Cartesian system

Table 2 Layout of dipolar.inp file.

INTEG WEIGHT VERBOSE n	INTEG - specifies which program was used for integration of electron density (Currently available AIMALL/XD) WEIGHT - if present specifies the use of weighting scheme (see text for more details) VERBOSE n (n=0,1,2) - setting n greater than 0 switches on extra printout to the bond.out file
nfiles	nfiles – number of files to be read into PolaBer from AIMALL/XD; nfiles=4 if calculations were done for EFIELD=0, X, Y, Z nfiles=7 if calculations were done for EFIELD=0, +/-X,+/-Y,+/-Z (highly recommended)
fname1 EFIELD EFX EFY EFZ fname2 EFIELD EFX EFY EFZ ...	fname – list of all AIMALL/XD file names (*.sum / *.out) with specification of applied electric field (EFFIELD) *i.e.* xp.sum EFIELD 0.005 0. 0. specifies output from AIMALL and applied EF in X direction with the value of 0.005 au
cell parameters 10.0000 10.0000 10.0000 90.000 90.000 90.000 0.0000 0.0000 0.0000 0.000 0.000 0.000	cell parameters given in Å in fractional coordinates with esd's
LATT N	lattice type, according with SHELX convention: 1=P, 2=I, 3=R_{obv} on hexagonal axes, 4=F, 5=A, 6=B, 7=C negative sign indicates non-centrosymmetric structure
SYMM x1 y1 z1 x2 y2 z2 x3 y3 z3, tx ty tz	symmetry operations within given space group x1,y1,z1 - 1st row of rotation matrix; x2,y2,z2 - 2nd row of rotation matrix; x3,y3,z3 - 3rd row of rotation matrix tx,ty,tz -translational components in decimal notation +/- 0.25, 0.33, 0.5, 0.67, 0.75
TYPE ntype	number of atom types
SFAC C H O	scattering factors for each type of atom
UNIT 10 10 10	number of atoms of each type in a unit cell, in SFAC order
LAMBDA 0.71073	wavelenght in Å
ATOMLIST	creates summary table for a chosen fragment
nlist	nlist - number of atoms to be included
at1 at2 ...	at1 at2 ... - list of atoms building chosen fragment for which summary table will be created in bond.out

Table 3 Components of atomic polarizability tensors of urea calculated with QTAIM partitioning based on B3LYP/6-311++G(2d,2p) calculations. All quantities are in atomic units (Bohr^3). Mol refers to the total molecular polarizability tensor.

Atom	α_{11}	α_{22}	α_{33}	α_{12}	α_{13}	α_{23}
C1	2.20	5.98	5.32	0	0	0.00
O2	4.85	4.72	12.89	0	0	0.00
N3	8.20	10.94	7.33	0	0	-3.36
H4	0.48	2.27	0.70	0	0	0.66
H5	0.52	0.66	2.60	0	0	-0.51
N6	8.20	10.94	7.33	0	0	3.36
H7	0.48	2.27	0.70	0	0	-0.66
H8	0.52	0.66	2.60	0	0	0.51
Mol	**25.43**	**38.44**	**39.48**	**0**	**0**	**0**

Table 4 Dielectric susceptibility and refractive indices for urea. Both quantities are dimensionless. Note that the crystal class of urea implies $\chi_{ij} = 0$ for $i \neq j$ and $\chi_{11} = \chi_{22}$

	χ_{11}	χ_{33}	n_o	n_e
a) Sum of gas phase molecular polarizabilities	0.821	1.012	1.349	1.418
+ Anisotropic Lorentz correction	1.131	1.526	1.460	1.589
+ rigorous local field Lorentz correction	1.119	1.571	1.456	1.603
+ rigorous local field Lorentz correction on distributed atomic polarizabilities	1.118	1.578	1.455	1.605
b) Sum of molecular polarizabilities from cluster calculation	0.943	1.207	1.394	1.486
c) Molecule in a polarizing continuum medium	1.170	1.510	1.473	1.584
Exp.* (extrapolated to infinite wavelength)			1.47	1.58

* Halbout *et al.* (1980)

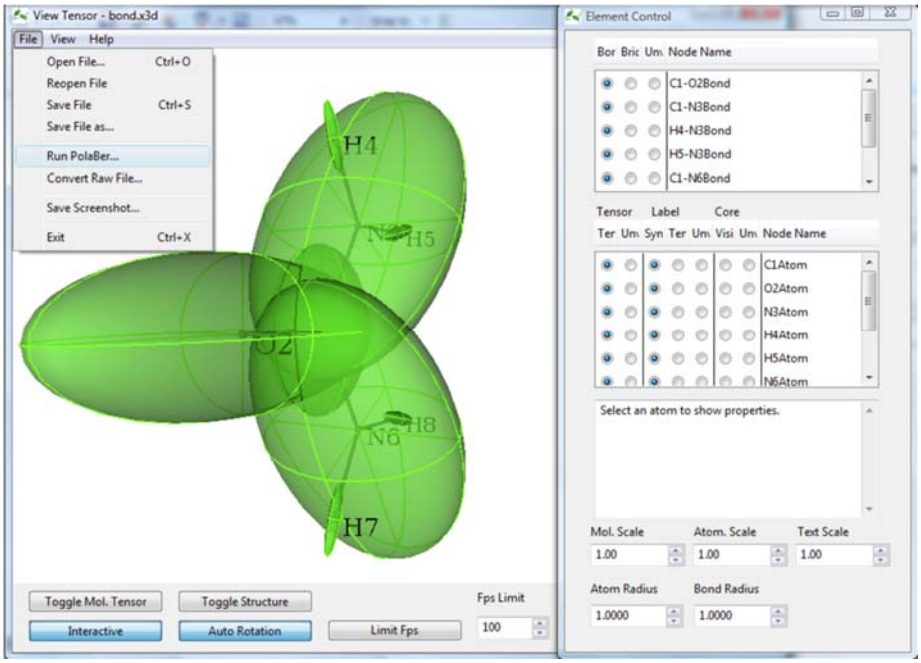

Figure 1 Graphical user interface for visualization of atomic polarizabilities and running PolaBer (available only on Windows platform).

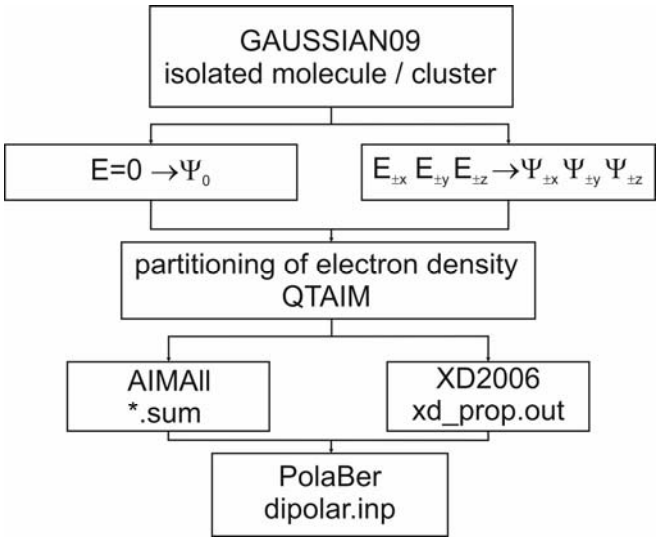

Figure 2 Schematic representation of necessary steps before entering PolaBer. E_i – applied electric field in a given direction; Ψ_I – wavefunction after applying external electric field.

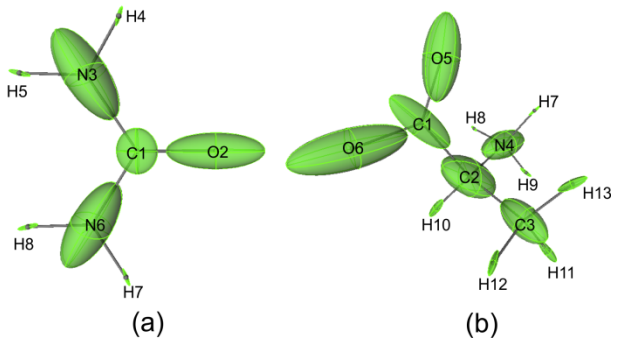

Figure 3 Graphical representation of distributed atomic polarizabilities for (a) urea and (b) L-alanine molecules. The scaling factor for atomic polarizabilities is 0.4Å^{-2}.

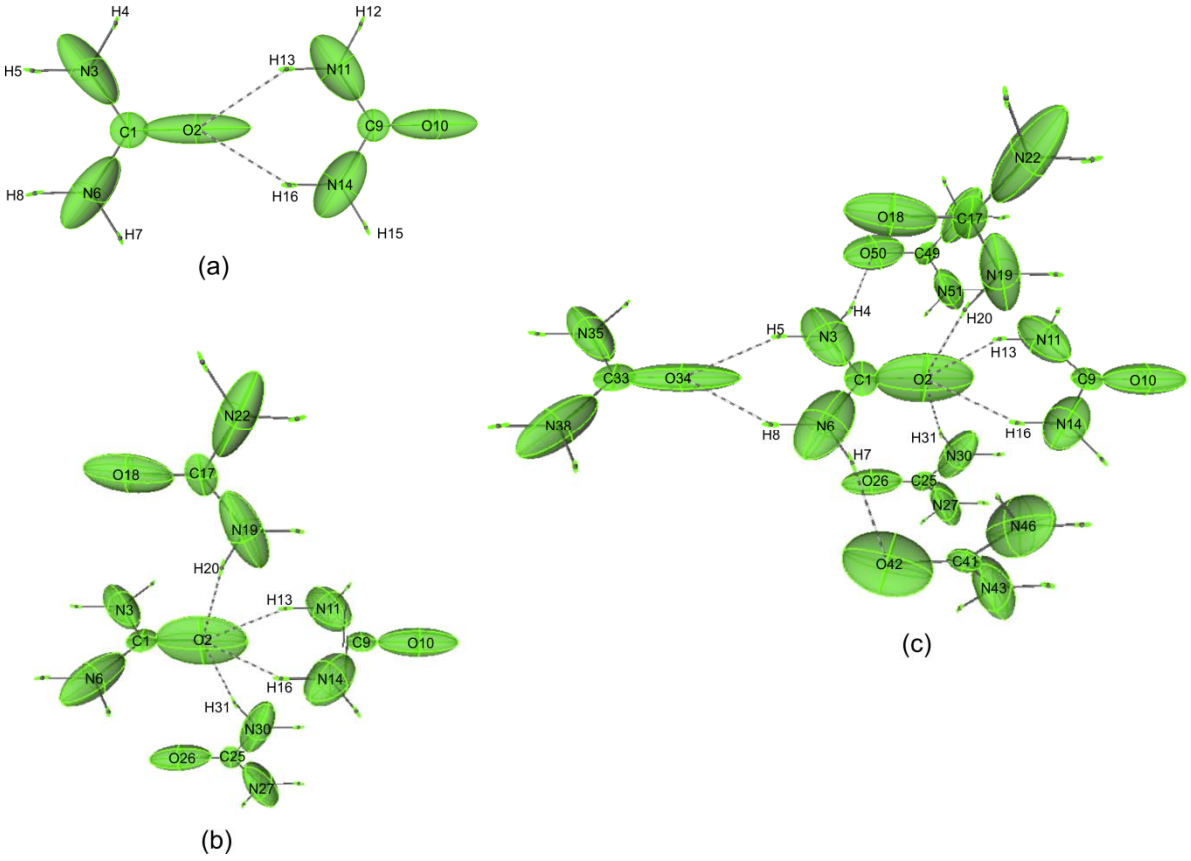

Figure 4 Graphical representation of atomic polarizabilities in case of supramolecular assemblies of urea. The scaling factor for atomic polarizabilities is 0.4Å^{-2}. Dashed lines indicate hydrogen bonds between molecules.

Supporting information

Table S1 **S**ummary of main quantities written in bond.out file obtained after calculations in PolaBer.

q(A)	Atomic charge (EFIELD=0*)
alpha11, alpha22, alpha33, alpha12, alpha13,alpha23	Components of atomic polarizability tensors ($Bohr^3$)
alphaiso	Isotropic value of atomic polarizability
Vol	Atomic volume bounded by an isosurface of the electron density distribution (0.001 a.u.Isodensity Envelope, EFIELD=0)
D(A-B)	Bond length in Bohr
d1, d2	Distances between atom A and BCP and BCP and atom B, respectively. (EFIELD=0, Bohr)
Rho, delrho, elips	Electron density, Laplacian and bond ellipticity(EF=0)
bcharge	Bond charge calculated for EFIELD=0
polA, polB, bonpol	Projections of polarizabilities of atom A on A-B bond and atom B on A-B bond, respectively bondpol=polA+polB (total bond polarizability)
dipA, dipB, bonddip	Projections of dipole moments of atom A on A-B bond and atom B on A-B bond, respectively bonddip=polA+polB (total bond dipole moment)
chi	Crystal electric susceptibility, obtained from summation of atomic polarizabilities in the crystal unit cell as well as from anisotropic Lorentz correction
n	Crystal refractive indices calculated from the crystal susceptibility. An analysis of the optic indicatrix is also provided.

* values corresponding to calculations without external electric field applied

Example of bash scripts using Gaussian09 for molecular orbital calculations, AIMAll for QTAIM analysis and PolaBer for atomic polarizabilities.

General Jobfile:

- choose the number of processors (-nproc) and number of atoms (-naat) computed at one time by AIMAll
- have g09, aimqb and polaber in the path
- have polar.gjf and dipolar.inp in the working directory
- g09 produce wfn file for each field calculation (zero.wfn, xp.wfn, xm.wfn etc.)

```
g09 < polar.gjf > polar.out
for fname in zero xp xm yp ym zp zm
do
  aimqb.ish -nogui -nproc=12 -naat=8 $fname.wfn
done
polaber
```

*Gaussian input file for calculating water distributed atomic polarizabilities (**polar.gjf**).*

- Set the number of processor (Nproc) for the molecular orbital calculation
- Choose the Hamiltonian and the basis set (in green)

```
%chk=polar.chk
%Nproc=12
#b3lyp/6-311++g(2d,2p) opt out=wfn

B3LYP 6-31++G(2d,2p) H2O

0 1
O       0.000000    0.000000    0.200000
H       0.000000   -0.500000   -0.700000
H       0.000000    0.500000   -0.700000

zero.wfn
--link1--
%chk=polar.chk
%Nproc=12
#b3lyp chkbasis nosymm scf=tight geom=checkpoint out=wfn
field=x+50

x=50

0 1

xp.wfn
--link1--
....
....
....
....
--link1--
%chk=polar.chk
%Nproc=12
#b3lyp chkbasis nosymm scf=tight geom=checkpoint out=wfn
field=z-50

z=-50

0 1

zm.wfn
```

Full reference for Gaussian09 program:

Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.